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Hydroxyl group rotation and hydrogen bonding in catechol : a PMR study

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Wide line PMR spectra at 7.5 Mc/S was recorded in the temperature range of 77°K–355°K. Hydrogen bonds are found to be strong enough to resist the molecular motion. The reduction in second moment with temperature suggests change in the composition of catechol.

1. Introduction

Present study was undertaken in an attempt to study the effect of a substituent hydroxyl group on the hydrogen bounding in di-ortho-substituted phenol. This study enables us to check the position of hydrogen atom coordinates, as well as the crystal structure.

Brown (1966) postulated the hydrogen atom coordinates of catechol. X-ray investigations by Brown revealed that the pairs of catechol molecules are related through the centre of symmetry and are linked together by means of the hydrogen bonds. There is also a possibility of the disorder of hydrogen bonds, depending upon the direction of hydrogen bond in the structure.

Catechol molecule is expected to be fairly dense as the hydrogen bonds draw the molecules together. There are also interactions between the two hydroxyl groups (Lloyd *et al* 1952). High resolution NMR studies (Batterhan *et al* 1964) showed that the introduction of the hydroxyl group at the ortho position in phenol has effect upon the hydroxyl group which is strongly hydrogen bonded.

2. Theoretical Calculations

(a) *Rigid lattice second moment* : The intra molecular (S_1) contribution to the second moment has been calculated by taking the hydrogen atom coordinates of Brown (1966) and using the modified Van Vleck's (1948) powder relation. S_1 was found to be 2.09 gauss^2.

Inter molecular (S_2) contribution to second moment has been calculated following the method of Andrew & Fades (1953) and was found to be 6.7 gauss^2.

This value of 6.7 gauss^2 is in reasonable agreement with the value of 6.9 gauss^2 calculated by Agarwal *et al* (1972) for the Pholoroglucinol molecule, which has a similar structure.

(b) *Calculation of reduction in second moment for the rotation of hydroxyl groups* : The OH group rotation would only affect the OH group contribution to the second moment. In present context only OH–OH contribution to the second moment would be affected. OH group rotation should reduce the OH group contribution to S_1 by a factor of 0.87 (Smith 1969). OH–OH contribution was found to be 1.79 gauss^2 and by OH group rotation, it will be reduced by 1.55 gauss^2. The reduced S_1 would be 0.44 gauss^2. If the OH group orientation causes approximately the same reduction in both the S_1 and S_2 then the S_2 would reduce to 1.30 gauss^2. Hence the reduced value of second moment for the rotation of both the hydroxyl groups would be 0.44+1.30 = 1.74 gauss^2.

3. Experiment and Results

The experiment was performed at the Varian's variable frequency spectrometer at the Tata Institute of Fundamental Research, Bombay. Second moments were derived from the derivative traces by using the trapezium rule. Modulation amplitude was kept small. The probable error in estimating second moment was found to be ± 0.85 gauss^2. Second moment *vs* temperature curve is shown in figure 1.

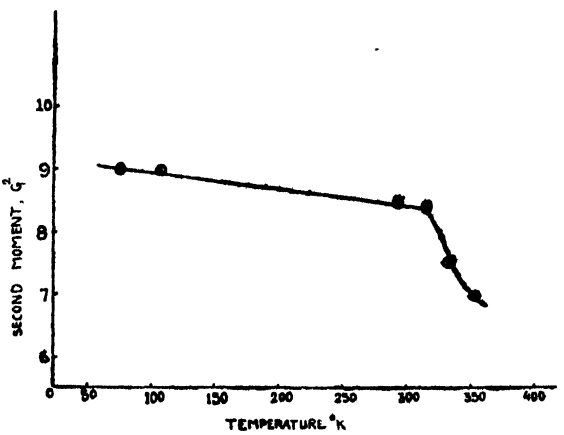

Fig. 1. Second moment *vs* temperature curve.

4. Discussion

Theoretically calculated value of the rigid lattice second moment comes out to be 8.79 gauss^2. This value agrees favourably with the experimental second moment at 77°K (9 gauss^2). The lattice is, therefore, rigid at 77°K.

The second moment calculations for the rigid lattice were made by using the hydrogen atom co-ordinates of Brown (1966). The consistency of our experimental and theoretical results at 77°K justify the hydrogen atom co-ordinates and crystal structure of Brown. The second moment roughly remains at the rigid lattice value upto a temperature of 312°K. After 312°K the second moment slightly decreases.

The helical hydrogen bonds bound the successive layers of the molecule around the crystallographic screw axis, it therefore, seems unlikely that the molecular rotation is taking place. The possibility of intramolecular rotation of hydroxyl group arises. Some fine structure was observed in catechol at about 312°K. Andrew (1951) observed that in some organic solids there is a decrease in the second moment below the transition temperature and stated that it is likely that the small portion of molecule is rotating below the transition temperature. Jatkar *et al* (1957) also found that the characteristic temperature of catechol is far below its melting point, thus indicating the presence of molecular motion in the solid state. But the observed second moment at 355°K (7.0 gauss^2) is incompatible with the calculated second moment (1.74 gauss^2) for the hydroxyl groups motion. Lloyd *et al* (1952) found two OH vibrational frequencies for the catechol, one corresponding to the bonded hydroxyl group and other corresponding to the free hydroxyl group. It may be possible that the free hydroxyl group may start rotation with the increase of temperature, while the other hydroxyl group remains strongly hydrogen bonded. For each such type of stationary rotating interactions the reduced value of second moment was found to be 3.89–4.79 gauss^2. But the observed second moment at 355°K does not agree with this value.

In the Phloroglucinol molecule (Trihydroxy substituted benzene) Agarwal *et al* (1972) found intramolecular hydroxyl group motion. The reason that we do not observe free rotation of hydroxyl groups in catechol may be that the rotation of hydroxyl group at the ortho position is hindered by the interactions with strongly hydrogen bounded hydroxyl group. Batterham *et al* (1964) also indicated that the substitution at the ortho position in phenol has greater interaction with the strongly hydrogen bounded hydroxyl group, than the substitution at the para position. Hence there is no free motion of the hydroxyl groups. Therefore, as the temperature rises hydroxyl group gains a tendency to rotate. But this tendency of hydroxyl group to rotate is nullified by the interactions with strongly hydrogen bonded hydroxyl group at the ortho position. The result is that the hydroxyl group at the ortho position tends to depart from planarity. This has also been supported by Roberts (1955). This departure from planarity with the rise of temperature may be the reason that the second moment slightly decreases by about 2 gauss^2.

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REFERENCES

Agarwal S. C., Mirza P., Agarwal V. D. & Gupta R. C. 1972 *Indian J. Pure & Appl. Phys.* **10**, 602.

Andrew E. R. 1951 *Physica* **17**. 405.

Andrew E. R. & Eades R. G. 1953 *Proc. Phys. Soc.* **A66**, 415.

Batterham T. J. & Highet R. J. 1964 *Australian J. Chem.* **17**, 428.

Brown, C. J. 1966 *Acta Cryst.* **21**, 170.

Jatkar S. K. K. & Deshpande C. M. 1957 *J. Univ. Poona, Sci. tech.* **No. 12**. 31.

Lloyd L. Ingraham Joseph Corse, Glen F. Bailey & Fed Still 1952 *J. Amer. Chem. Soc.* **74**, 2297.

Roberts E. A. H. 1955 *Chemistry and Industry* 1551.

Smith G. W. 1969 *J. Chem. Phys.* **50**, 3595.

Van Vleck J. H. 1948 *Phys. Rev.* **74**, 1168.